



Carbon riveted PtRu/C catalyst from glucose in-situ carbonization through hydrothermal method for direct methanol fuel cell



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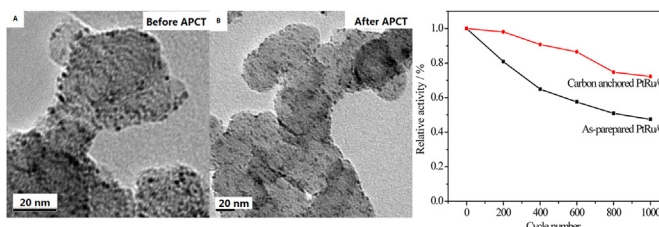
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HIGHLIGHTS

- PtRu/C nanoparticles are riveted through glucose in-situ carbonization by hydrothermal method.
- The durability of carbon riveted PtRu/C increases one time and also its activity enhances 6%.
- Carbon nanolayer on the support surface inhibits the migration and coalescence of PtRu particles.
- Increasing of Pt(0), Ru(0) and carbon groups on surface of riveted PtRu/C enhance its durability.

GRAPHICAL ABSTRACT



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ABSTRACT

PtRu/C catalyst is synthesized by microwave-assisted polyol process. Then, the PtRu nanoparticles are riveted through glucose in-situ carbonization by hydrothermal method. X-ray diffraction, transmission electron microscopy, cyclic voltammograms, CO_{ad} stripping voltammetry, electrochemical impedance spectroscopy and accelerated potential cycling tests have been carried out to characterize their properties. The experimental results indicate that the average sizes of PtRu nanoparticles grow up from 1.54 nm to 2.56 nm after hydrothermal method. The electrochemical active specific surface areas of as-prepared and carbon riveted PtRu/C are 73.0 m² g⁻¹ Pt and 89.6 m² g⁻¹ Pt, respectively. The durability of carbon riveted PtRu/C increases one time after APCT of 1000 cycles and its mass activity also enhances 6% in first cycles in comparison with that of as-prepared PtRu/C. An enhanced stability of carbon riveted PtRu/C is mainly attributed to the existence of carbon nanolayer on the surface of the support from glucose in-situ carbonization to inhibit the migration and coalescence of PtRu nanoparticles on the support during work. Besides, the increased ratio of Pt(0), Ru(0), and carbon groups with higher stability and the evidently decreased of PtO₂ and RuO_xH_y on surface of carbon riveted PtRu/C is another important reason to enhance its durability.

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1. Introduction

Direct methanol fuel cell (DMFC) is a competitive electrochemical device in portable power source, for its several advantages, such as its light weight, high energy density, and safety in

transporting, environmentally nonpolluting products and simplified system design [1–7]. Among various of anodic catalysts for DMFC, the PtRu/C catalyst is commonly used because of its capability to remove absorbed CO or the reaction intermediate which forms during methanol electro-oxidation [8,9].

However, the durability of PtRu/C catalyst still cannot meet the demand of the long-term operation [10,11]. The main reason is metal nanoparticles' loss and Ostwald growth due to PtRu metal

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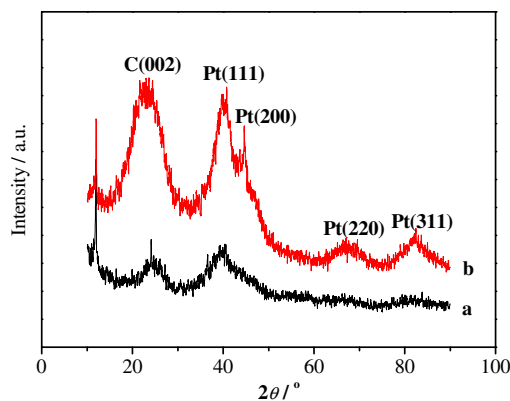


Fig. 1. XRD patterns of as-prepared PtRu/C catalyst (a) and carbon riveted PtRu/C catalyst (b).

dissolution, and also the corrosion of carbon support at high voltages [12–15]. By now, many researchers put forward three ways to enhance the stability of PtRu/C catalyst [16]. First is to make highly stable PtRu structures. The performances of f.c.c. PtRu solid solutions are much higher than those of Ru oxide/hydroxide and h.c.p. PtRu solid solutions during long-term fuel cell operation [17,18]. Hu et al. [19] thought that suitable thermal treatments can increase the stability of PtRu catalyst. When the RuO_xH_y annealed at 350 °C, PtRu catalyst shows the excellent stability. Second is through the use of suitable supports. Wang et al. [20] deposited PtRu nanoparticles onto 1-aminopyrene (1-AP)-functionalized MWCNTs by a

microwave-assisted polyol process. And it was found that the PtRu nanoparticles on 1-AP-functionalized MWCNTs enhanced their stability for methanol electrooxidation in acid solution than those on acid-oxidized MWCNTs and XC-72 carbon black. Finally, the stability of the catalyst can also be increased by adding the stabilizing agents. Liang et al. [21] prepared an Au-modified PtRu catalyst (Au/PtRu) and found that the incorporation of Au could significantly stabilize the PtRu nanoparticles through the prevention of the dissolution of Ru metal.

However, all of those ways have their limitations and thus cannot be widely used. In our previous work, the carbon riveted Pt/C catalyst was designed and prepared by glucose in-situ carbonized by heat treatment [15]. However, this method is carried out at 400 °C, which resulted in the remarkable increasing of Pt nanoparticles during treatment. In this work, to further increase the catalyst's stability and activity of PtRu nanoparticles during treatment, carbon nanolayer was first formed on surface of the PtRu/C catalyst through glucose in-situ carbonization through hydrothermal method. It will be a promising method for application to DMFC.

2. Experimental

2.1. Catalysts preparation

In the present studies, all chemicals were analytical reagent. Hexachloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) and ruthenium chloride (RuCl_3) were purchased from Beijing, China. Vulcan XC-72 carbon black with mean particle size of 20 nm was purchased from Cabot and 5 wt.% Nafion solution was obtained from Dupont. The PtRu/C

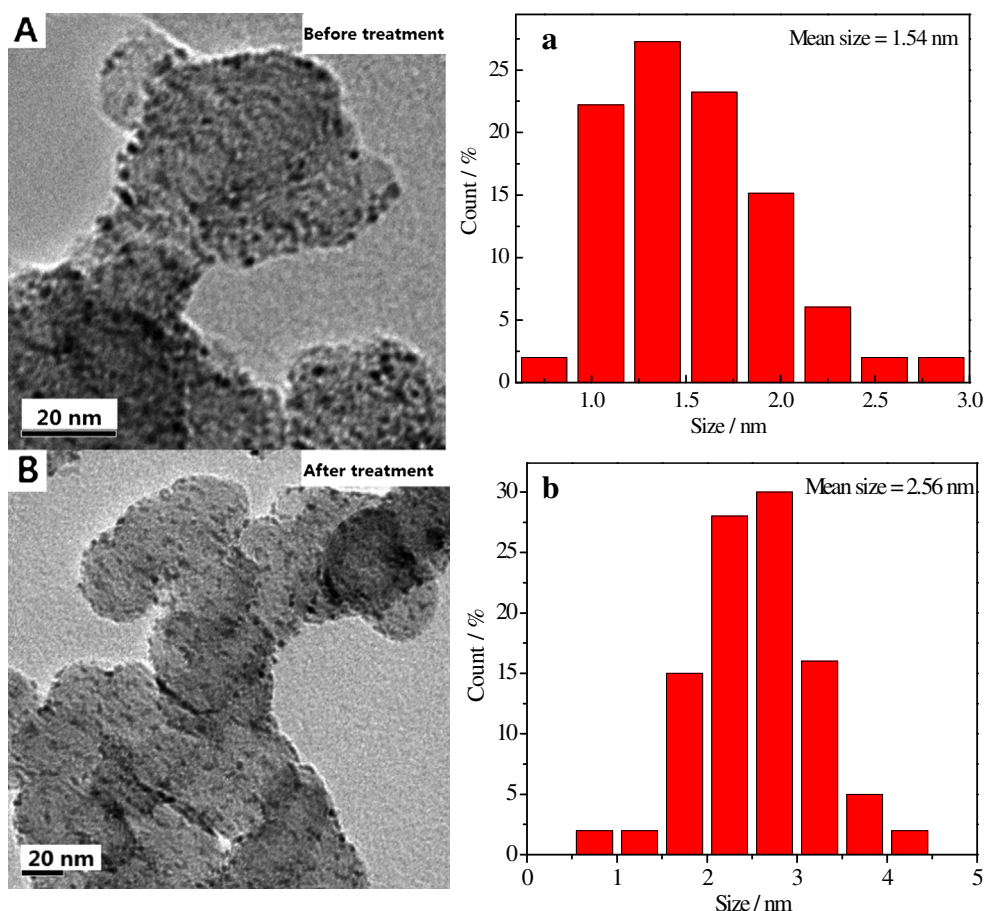


Fig. 2. TEM images and the distribution of the particle size of as-prepared PtRu/C catalyst (a) and carbon riveted PtRu/C catalyst (b).

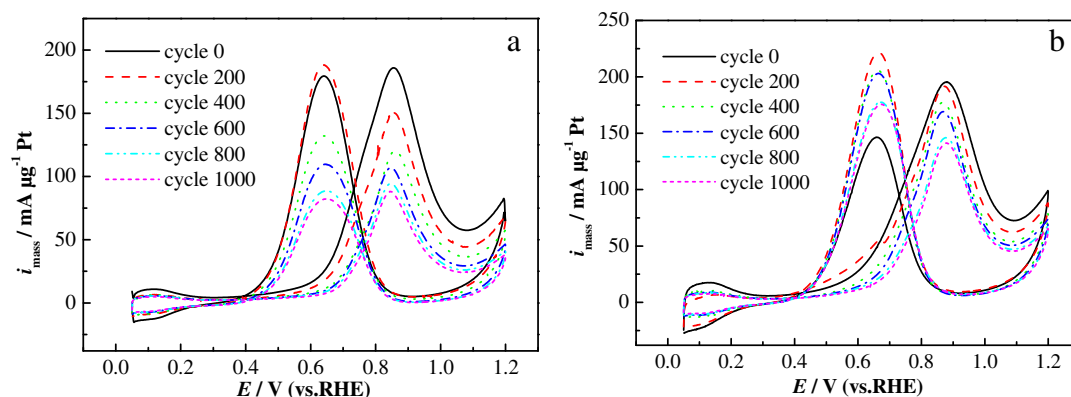


Fig. 3. The cyclic voltammograms of CH_3OH electrooxidation with mass activity, $i_{\text{mass}}/\text{mA } \mu\text{g}^{-1} \text{Pt}$ (current density per mass of Pt loaded), on as-prepared PtRu/C catalyst (a) and carbon riveted PtRu/C catalyst (b) during the 1000 cycles. Scanning rate: 50 mV s^{-1} .

(metal loading of 20 wt.% supported XC-72R, Cabot) catalyst was prepared through a microwave-assisted polyol process (MAPP) [22,23] and the atomic ratio of Pt/Ru was adjusted to that of the commercial catalyst (atomic ratio of 1:1). Briefly, a calculated amount of XC-72R carbon black was dispersed into mixture of ethylene glycol and isopropyl alcohol under ultrasonic treatment for 1 h. After the suspension was stirred for 3 h, a selected amount of $\text{H}_2\text{PtCl}_6\text{-EG}$ and $\text{RuCl}_3\text{-EG}$ solution was added into the uniform carbon ink drop by drop with urgent agitation for 3 h. Followed by adjusting the pH (pHS-32 m) to 8 by using a $1 \text{ mol L}^{-1} \text{NaOH}$ ethylene alcohol solution, the suspension was subjected to consecutive microwave heating for 50 s in a microwave oven (from Galanz Ltd., 800 W) under flowing Ar. After the solution was cooled to room temperature, pH was adjusted to 2 by HNO_3 aqueous solution, which was then stirred for 12 h. Finally, the product was filtered, washed for several times with ultrapure water (Millipore, $18.2 \text{ M}\Omega \text{ cm}$). The obtained PtRu/C catalysts were dried for 3 h at 80°C and then were stored in a vacuum vessel.

The as-prepared PtRu/C was riveted by carbon nanolayer forming glucose in-situ carbonization through hydrothermal method. In brief, after a calculated amount of as-prepared PtRu/C and glucose (6% mass ratio of carbonized carbon from the carbonization of glucose to the PtRu/C catalyst) was dispersed into ultrapure water under ultrasonic treatment, the catalyst ink was put in a reaction kettle (from Dalian, China). Then, before the carbonization of glucose at 160°C for 4 h, the air in kettle was eliminated by high-pure argon. After it was cooled to room temperature, the carbon riveted PtRu/C catalyst was washed, dried, and stored in vacuum.

2.2. Physical characterization

2.2.1. X-ray diffraction (XRD)

The D/max-RB diffractometer (made in Japan) using a Cu K α X-ray source operating at 45 kV and 100 mA, scanning at a rate of 4° min^{-1} with an angular resolution of 0.05° was used to obtain the XRD patterns of all catalysts.

2.2.2. Transmission electron microscopy (TEM)

TEM pictures of all catalysts were characterized by using a TECNAI G2 F30 field emission transmission electron microscope operated at 300 kV. The samples for TEM analysis were prepared by ultrasonically dispersing the catalyst powder in ethanol. A drop of the suspension was deposited on a standard copper grid coated with carbon film. The copper grid was then dried overnight.

2.2.3. X-ray photoelectron spectroscopy (XPS)

To determine the surface properties of the catalysts, XPS analysis was carried out by using the Physical Electronics PHI model 5700 instrument. Before XPS analysis, all samples were dried under vacuum at 80°C overnight. The take-off angle of the sample to analyzer was 45° and the Al X-ray source was operated at 250 W. Survey spectra were collected at a pass energy (PE) of 187.85 eV over a binding energy range from 0 eV to 1300 eV. High binding energy resolution multiplex data for the individual elements were collected at a PE of 29.55 eV. During all XPS experiments, the pressure inside the vacuum system was maintained at $1 \times 10^{-9} \text{ Pa}$.

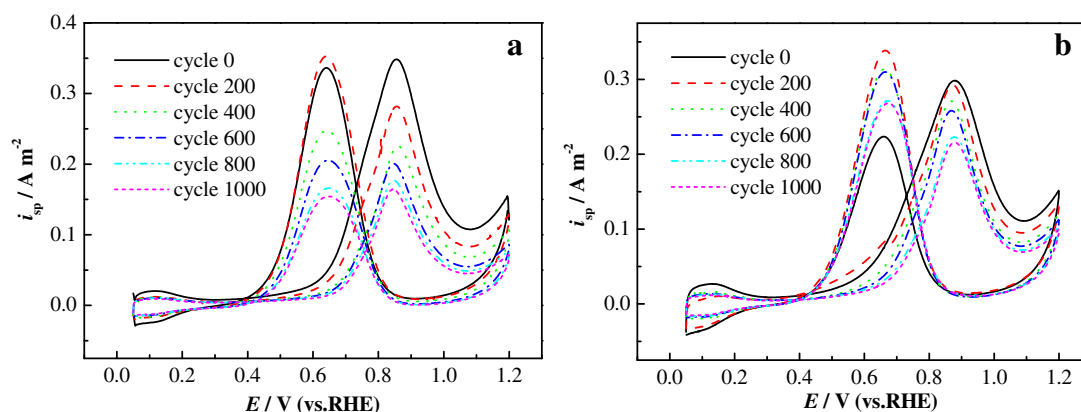


Fig. 4. The cyclic voltammograms of CH_3OH electrooxidation with specific activity, $i_{\text{sp}}/\text{A m}^{-2}$ (current density per electrochemical active specific surface area), on as-prepared PtRu/C catalyst (a) and carbon riveted PtRu/C catalyst (b) during the 1000 cycles. Scanning rate: 50 mV s^{-1} .

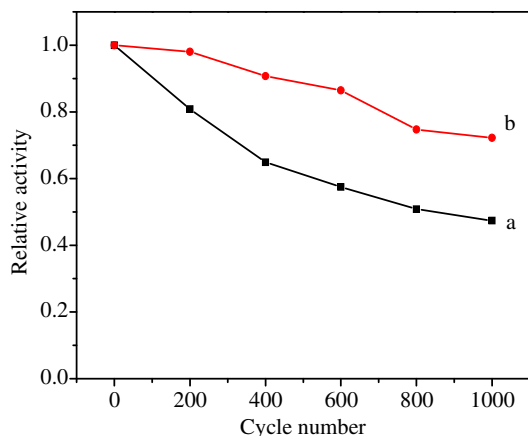


Fig. 5. Relationship of relative activity and cycle number during the test: as-prepared PtRu/C catalyst (a) and carbon riveted PtRu/C catalyst (b).

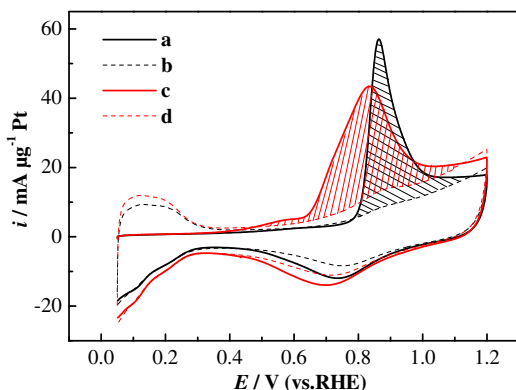


Fig. 6. The CO_{ad} stripping voltammetry on as-prepared PtRu/C catalyst (a, b) and carbon riveted PtRu/C catalyst (c, d). Scanning rate: 50 mV s^{-1} .

2.3. Electrochemical measurements

Electrochemical measurements were performed using a CHI 650D potentiostat and a conventional three-electrode electrochemical cell. The counter electrode was Pt sheet of 1 cm^2 plate and a $\text{Hg}/\text{Hg}_2\text{SO}_4$ electrode (-0.68 V relative to reversible hydrogen

electrode, RHE) was used as the reference electrode. The as-prepared PtRu/C and carbon riveted PtRu/C catalyst electrodes were used as the working electrode. The catalyst ink was prepared by ultrasonically dispersing catalyst powders in an appropriate amount of ultrapure water. The catalyst ink of $5 \mu\text{L}$ was dropped onto a glassy carbon working electrode, and was dried for 15 min. Later, $5 \mu\text{L}$ of Nafion solution (5 wt.%) was spread on the surface of electrode, and dried in air. In all cases, the total loading of metal was $28 \mu\text{g cm}^{-2}$.

The electrochemical measurements of the catalysts were carried out in a glass cell containing $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ and $0.5 \text{ mol L}^{-1} \text{ CH}_3\text{OH}$ solution at $25 \pm 1^\circ \text{C}$. Highly purified argon gas was purged into the solution for 20 min to eliminate oxygen.

And the long-term stability of the catalyst was measured by a continuous 1000 potential cycling between 0.05 V and 1.20 V (vs. RHE) with a scanning rate of 50 mV s^{-1} . All potentials are reported with respect to normal hydrogen electrode in this paper.

The electrochemical active surface area of PtRu/C catalyst was determined by CO_{ad} stripping voltammetry, assuming the formation of a monolayer of linearly adsorbed CO and the coulombic charge required for oxidation of CO_{ad} to be 420 mC cm^{-2} . The voltammetry was carried out in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ at 25°C with a scanning rate of 50 mV s^{-1} .

Electrochemical impedance spectroscopy (EIS) was obtained at frequencies between 100 kHz and 0.01 Hz with 12 points per decade. The amplitude of the sinusoidal potential signal was 5 mV . Due to a slight interference from the Nafion film, the working electrode was electrochemically cleaned by continuous cycling at 50 mV s^{-1} until a stable response was obtained before the measurement curves were recorded.

3. Results and discussion

The XRD patterns of the as-prepared PtRu/C and carbon riveted PtRu/C catalysts are shown in Fig. 1. In each XRD pattern, besides the diffraction peak of C(002) at 24.7° , the 2θ values of the other four peaks correspond to the (111), (200), (220), and (311) crystal planes of crystalline face-centered cubic Pt. And it can be seen from Fig. 1 that the XRD patterns of two PtRu/C catalysts are obviously different, which indicate that the average sizes and relative crystallinity of the PtRu nanoparticles have been notably changed after carbon anchor through hydrothermal method, the crystallinity of the carbon riveted PtRu/C catalyst is evident higher than that of as-prepared PtRu/C.

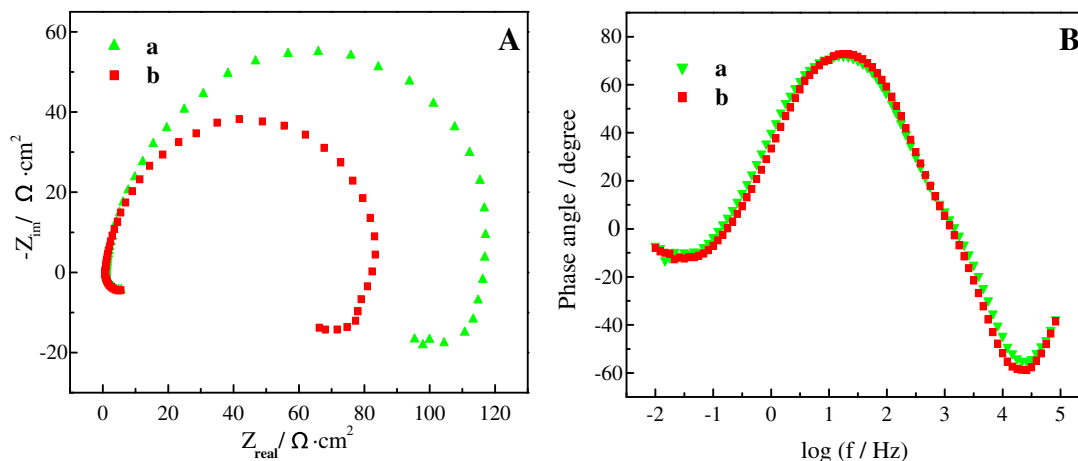


Fig. 7. Impedance patterns (A) and phase shift plots (B) of methanol electrooxidation in an Ar-saturated solution of $0.5 \text{ mol L}^{-1} \text{ CH}_3\text{OH}$ and $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ at 25°C on the as-prepared PtRu/C catalyst (a) and carbon riveted PtRu/C catalyst (b) at a potential of 650 mV .

Fig. 2 shows the TEM images of as-prepared PtRu/C and carbon riveted PtRu/C catalysts and their size distribution of PtRu nanoparticles. As is seen from Fig. 2, the PtRu nanoparticles of the two catalysts are highly dispersed and their average particle sizes are 1.54 nm and 2.56 nm, respectively. After the treatment, the particle

size of PtRu/C catalyst evidently increases, which indicates that the hydrothermal method also leads to the increasing of particles size of PtRu catalyst to some degree.

The activity and stability of two catalysts is determined by accelerated potential cycling tests (APCT) of a continuous 1000

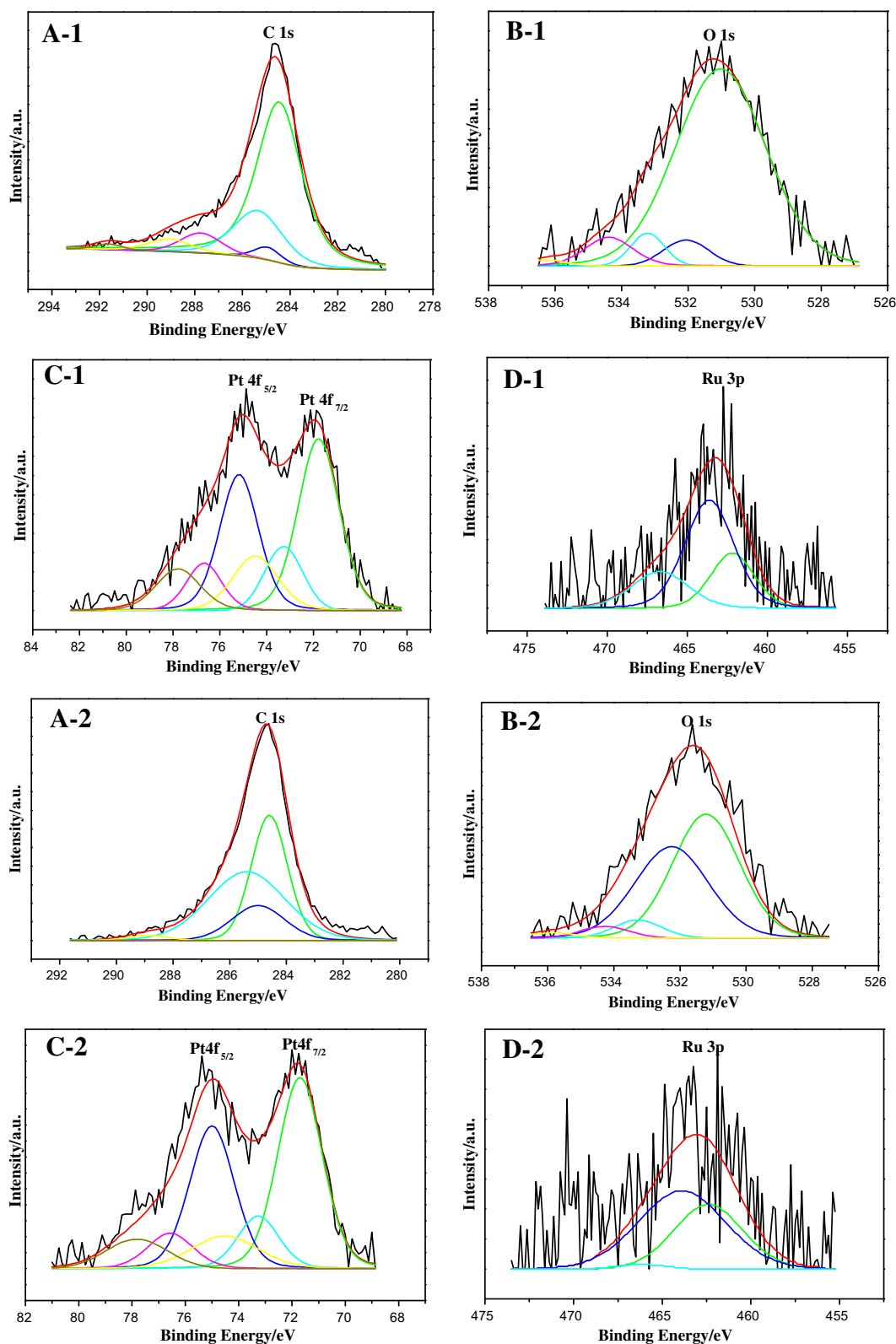


Fig. 8. Deconvoluted Pt 4f (C-1, C-2), Ru 3d (D-1, D-2), C 1s (A-1, A-2) and O 1s (B-1, B-2) peaks from XPS analysis of as-prepared PtRu/C (A-1, A-2, A-3, A-4) catalyst and riveted PtRu/C (B-1, B-2, B-3, B-4) catalyst.

potential cycles between 0.05 V and 1.2 V with a scanning rate of 50 mV s⁻¹ Fig. 3 shows the CV curves of methanol electrooxidation on each catalyst electrode during the potential cycling. Their mass activities, $i_{\text{mass}}/\text{mA } \mu\text{g}^{-1}$ (current density per mass of Pt loaded), of as-prepared and carbon riveted PtRu/C catalysts in first cycles are 184.4 and 195.5 mA μg^{-1} , respectively, which indicates that the mass activity of the latter slightly increases by 6%.

Their specific activities, $i_{\text{sp}}/\text{A m}^{-1}$ (current density per electrochemical active specific surface area), are shown in Fig. 4. The initial specific activity of the catalyst reduced approximately 14% from 0.35 A m⁻¹ to 0.30 A m⁻¹ after the treatment. Compared with the growth of mass activity, the decreased specific activity should be attributed to the difference of turnover frequency (TOF) between as-prepared and carbon riveted PtRu/C catalysts.

Their stability is compared by using the loss of current density, which is under the forward scan at peak potential. To present the stability of two catalysts more clearly, the relationship of current density and cycle number during APCT is presented in Fig. 5. As is shown in Fig. 5, the current densities decrement of as-prepared PtRu/C and carbon riveted PtRu/C at first peak potential is 52.6% and 27.8%. Their specific activities are 0.16 A m⁻¹ and 0.22 A m⁻¹, respectively, after 1000 cycles as shown in Fig. 4. Although carbon riveted PtRu/C is 14% lower at the first cycle than that of as-prepared PtRu/C, the latter is 37.5% higher than the former after 1000 cycles. The results illustrate that carbon nanolayer forming from glucose in-situ carbonization through hydrothermal method can significantly increase the stability of PtRu/C catalyst, almost enhance one time.

Fig. 6 shows the CO_{ad} stripping voltammograms for as-prepared PtRu/C and carbon riveted PtRu/C catalysts. Both the onset potential and peak potential for the oxidation of adsorbed CO on carbon riveted PtRu/C catalyst shift to a lower electrode potential after hydrothermal treatment in comparison with those on as-prepared PtRu/C. The potentials shift to a lower electrode potential must originate from the facts that the size of PtRu nanoparticles increase [24,25] and the surface ratio of Pt and Ru is more appropriated for electrooxidation of adsorbed CO molecules on carbon riveted PtRu/C catalyst after hydrothermal treatment. The electrochemical active specific surface areas of the as prepared and carbon riveted PtRu/C catalysts calculated by CO_{ad} stripping voltammetry are 73.0 m² g⁻¹ Pt and 89.6 m² g⁻¹ Pt, respectively. Its increased electrochemical active surface area ascribes the large extent of alloying agree of Pt with Ru and the surface content of bare Pt increases to result into the increasing of Pt atoms being suitable for the adsorption CO molecules.

The EIS (A) and the phase shift (B) on the as-prepared PtRu/C and carbon riveted PtRu/C catalysts in an Ar-saturated solution of 0.5 mol L⁻¹ CH₃OH and 0.5 mol L⁻¹ H₂SO₄ at 25 °C at 650 mV are shown in Fig. 7. The Faradaic admittance (the inverse of the Faradaic impedance) of methanol electrooxidation is [26]:

$$Y_F = \frac{1}{R_{\text{ct}}} + \frac{B}{a + j\omega} \quad (1)$$

where $R_{\text{ct}} = (\partial E / \partial I_F)_{\text{ss}}$ is charge transfer resistance of the electrode reaction. Its value is always positive. The subscript “ss” stands for steady state. I_F denotes the Faraday current. It can be seen from Fig. 7A that the reaction resistances (R_{ct}) for methanol electrooxidation on the carbon riveted PtRu/C catalyst is evidently smaller than that of the as-prepared PtRu/C catalyst. It reveals that the rates of oxidation removal of the CO_{ad} by OH_{ad} are rapid on the riveted catalyst. Two coincident curves can be observed in Fig. 7B, indicating that the reaction mechanism of methanol electrooxidation on the two catalysts is the same.

Table 1
Results of the fits of the Pt4f spectra.

Catalysts	Species	Orbital spin	Binding energy/eV	Peak half width/eV	Assignment	Relative content/%
As-prepared PtRu/C	Pt 4f	4f _{7/2}	71.78	2.07	Pt	34.34
		4f _{5/2}	75.18	1.96	Pt	25.73
		4f _{7/2}	73.28	1.92	PtO	10.81
		4f _{5/2}	76.68	1.77	PtO	8.08
		4f _{7/2}	74.49	2.29	PtO ₂	12.05
		4f _{5/2}	77.79	2.24	PtO ₂	8.99
Riveted PtRu/C	Pt 4f	4f _{7/2}	71.70	1.96	Pt	37.49
		4f _{5/2}	75.00	1.98	Pt	28.14
		4f _{7/2}	73.27	1.83	PtO	9.63
		4f _{5/2}	76.57	2.04	PtO	7.28
		4f _{7/2}	74.52	3.00	PtO ₂	9.98
		4f _{5/2}	77.82	2.72	PtO ₂	7.48

The XPS measurements performed with as-prepared PtRu/C and carbon riveted PtRu/C samples are to explore the reasons of the enhanced stability. Fig. 8 shows the XPS spectra in the binding energy ranges of Pt4f, Ru3p, C1s, and O1s for as-prepared PtRu/C and carbon riveted PtRu/C catalysts. Further information such as species, binding energy and peak half width, can be found in Tables 1–4

The quantitative area ratios of Pt, PtO and PtO₂ are presented in Table 1. As is shown in Table 1, the ratios of each Pt species, Pt(0), Pt(II), Pt(IV) in carbon riveted PtRu/C catalyst are 65.63%, 16.91% and 17.46%, respectively, and which in the as-prepared PtRu/C catalyst are 60.07%, 18.89% and 21.04%. As we know, Pt(0) is a kind of very stable metal, which is hard to be oxidized in electrochemical environment. However, Pt(II) and Pt(IV) can be easily reduced by reductant and then redeposited onto carbon paper during the operation of DMFC. Accordingly, Pt(0) is much stabler than Pt(II) and Pt(IV) in electrochemical environment. The results of the fits of Pt4f spectra indicate that the increasing of Pt(0) relative to Pt(II) and Pt(IV) on the surface of the carbon riveted catalyst is one of the reasons for its improvement durability.

Table 2 is the result of the fits of the Ru 3p spectra. The ratio of the Ru(0) increases from 24.54% to 38.58% after glucose in-situ carbonization, and those are similar to the results of Pt4f. Therefore, it should be another reason for the improvement stability of carbon riveted PtRu/C after carbon riveted treatment. From the results above, carbon nanolayer from glucose in-situ carbonization may also reduce the Pt and Ru oxides to metal, which ought to result in the increasing of Pt(0) and Ru(0) ratio on the surface of carbon riveted PtRu/C catalyst.

To compare the ratios of oxygen species, the main oxygen species on the surface of the as-prepared PtRu/C and carbon riveted PtRu/C catalysts are shown in Table 3. It is found that hydroxyl group increases from 5.16% to 40.47%. Table 4 is the result of the fits of the C1s spectra. It can be seen from Table 4 that the ratio of sp³ hybridization carbon and C–OR groups on the surface of carbon riveted PtRu/C catalyst from glucose in-situ carbonization evidently increased, indicating that carbon nanolayer has good corrosion

Table 2
Results of the fits of the Ru3p spectra.

Catalysts	Species	Orbital spin	Binding energy/eV	Peak half width/eV	Assignment	Relative content/%
As-prepared PtRu/C	Ru 3p	3p _{1/2}	462.18	3.20	Ru	24.54
		3p _{1/2}	463.62	3.60	RuO ₂	54.02
		3p _{1/2}	466.70	4.20	RuO _x H _y	21.44
		3p _{1/2}	462.40	4.60	Ru	38.58
Riveted PtRu/C	Ru 3p	3p _{1/2}	463.90	5.80	RuO ₂	59.05
		3p _{1/2}	466.20	3.60	RuO _x H _y	2.37

Table 3

Results of the fits of the O1s spectra.

Binding energy/eV	531.20 (–C=O)	532.25 (–OH)	533.30 (R–O–R)	534.30 (–COOH)	539.90 (H ₂ O)
As-prepared PtRu/C	82.24	5.16	4.89	6.68	1.03
Riveted PtRu/C	49.79	40.47	5.08	3.25	1.42

Table 4

Results of the fits of the C1s spectra.

Catalysts	Species	Bond	Binding energy/eV	Peak half width/eV	Relative content/%
As-prepared PtRu/C	C 1s	sp ² –C	284.45	2.23	65.43
		sp ³ –C	284.95	1.30	2.78
		C–OR	285.35	2.45	19.78
		C=O	287.75	2.00	6.40
		COOR	289.07	2.13	4.46
Riveted PtRu/C	C 1s	π	291.61	1.33	1.15
		sp ² –C	284.60	1.50	38.03
		sp ³ –C	285.00	2.19	15.63
		C–OR	285.40	3.20	44.40
		C=O	288.30	1.68	0.04
		COOR	288.89	1.68	1.74
		π	289.03	1.78	0.16

resistance, which is another reason for the improvement durability of carbon riveted PtRu/C catalyst.

4. Conclusions

In this work, the carbon riveted PtRu/C catalyst was obtained by first microwave-assisted polyol process, and then treated through hydrothermal method. The experimental results show that the durability of carbon riveted PtRu/C catalyst enhanced one time in comparison with that of as-prepared PtRu/C, and the mass activity of the former is slightly higher than that of the latter. The enhanced mass activity of carbon riveted PtRu/C catalyst lies in the surface ratio of Pt and Ru which is more appropriated for electrooxidation of adsorbed CO molecules and the surface content of bare Pt increases to result into the increasing of Pt atoms being suitable for the adsorption CO molecules. The significantly enhanced stability for carbon riveted PtRu/C catalyst is attributed to two critical reasons: (1) the anchoring effect of carbon nanolayer formed during the glucose in-situ carbonization through hydrothermal method; (2) the content increasing of Pt (0), Ru(0), sp³ hybridization carbon and C–OR groups composition and the evidently decreasing PtO₂

and RuO_xH_y after the carbon riveted process. Full tests of these supported catalysts in single fuel cell under high-temperature conditions are still in process.

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